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X-RAY DIFFRACTION STUDY OF INTERATOMIC CORRELATIONS IN ALLOYS WITH COMPONENTS HAVING CLOSE ATOMIC NUMBERS (Cu–Zn and Cu–Ni)

A. A. Katsnelson, V. M. Silonov, T. V. Skorobogatova, and O. V. Kris'ko

By the method of X-ray diffuse scattering, a short-range order in Cu–Zn alloys and short-range stratification in Cu–Ni alloys have been established.

The presence of a short-range order has been established in some 70 binary and multicomponent solid solutions by direct X-ray diffraction methods. A peculiar feature of the alloys that have been studied is that there is a significant difference (by 10 or more) in the atomic numbers of their components. Alternatively, alloys whose components have close atomic numbers are known to have a wide application in technology. Until recently, the fine structure of such alloys has not been studied by direct X-ray methods. A few publications are only available on neutron diffraction analyses performed on alloys composed of components with close atomic numbers [1–3]. This is due to that performance of a neutron diffraction experiment involves some difficulties. As a rule, such systems have been studied by indirect methods, for example, by measuring electrical resistance, thermal e. m. f. or other techniques. Anomalies in physical properties observed in the experiments were interpreted based on the notions on a short-range order whose type cannot be considered established unless special experiments are made. No X-ray diffraction studies of a short-range order have so far been carried out on alloys whose components have close atomic numbers. This can be explained by the fact that the atoms of such components do not differ much in their scattering power and, hence, modulation of the Laue background is weak. Nevertheless, the results of application of the fluctuation wave theory [4] to polycrystalline alloys [5] and the study of the effect produced by static lattice distortions on the diffuse scattering of X-rays [6–8] indicate that if atomic volumes differ, the X-ray diffuse scattering caused by the size effect is significant and provides information on interatomic correlations even if the atomic numbers of the components are close.

This paper presents the results of our study of X-ray diffuse scattering in the Cu–15 at.% Zn and Cu–15 at.% Ni alloys. A technique is proposed for processing the experimental data to determine the short-range order parameters in solid solutions that contain atoms with close numbers but different volumes (i. e. when the size effect is essential). The results obtained are in agreement with neutron diffraction data published in the literature.

EXPERIMENTAL

In this study, the intensity of X-ray diffuse scattering was measured by a DRON diffractometer using Cu-K_α radiation monochromatized by a Si flat single crystal. Scattered radiation was recorded by a scintillation counter. The intensity of thermal diffuse scattering was computed using theory [9], and that of Compton scattering was estimated as described in [10]. The values of characteristic temperatures, atomic scattering factors, scatter corrections, and elastic constants were taken from [10–12]. The measurements were performed in a broad range of angles (up to $2\theta = 140$ deg) so as to take account of scattering due to a quadratic size effect which is rather significant at large angles. At the same time, as is known, large scattering angles are associated with substantial scattering caused by thermal motion of atoms. The intensity formula presented in [9] describes, to sufficient accuracy, the contribution of thermal diffuse scattering to experimental data. However, as is known, the characteristic temperature Θ_D [13] may differ from Θ_D obtained in measuring the heat capacity. For this reason, a specific analysis is required to estimate the contribution of thermal diffuse scattering. To do this, diffuse scattering of pure copper was first measured.

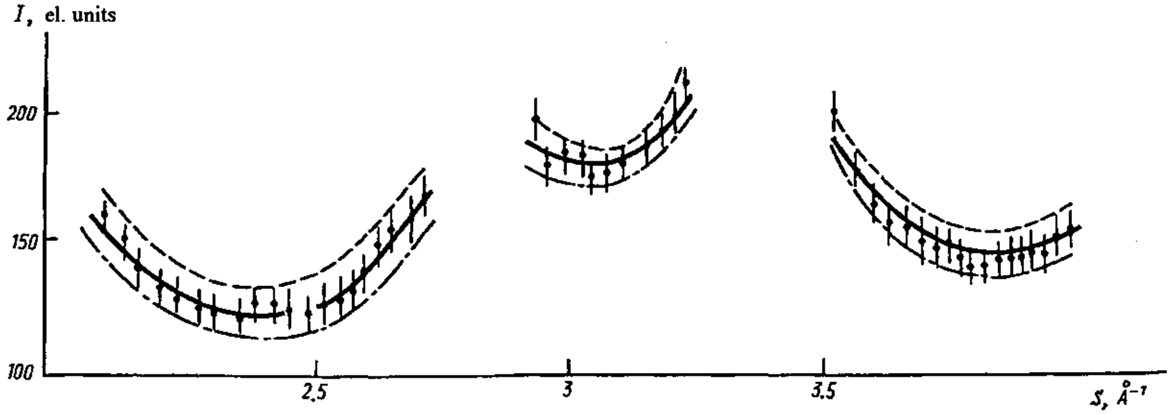

Fig. 1

Intensity of X-ray diffuse scattering in copper plotted vs. $S = 4\pi \sin\theta/\lambda$: experiment (dots) and computation at $\Theta_D = 320$ K (dashed), 330 K (solid), and 340 K (dash-and-dot).

Comparison of the experimental and theoretical values of the intensities suggests (Fig. 1) that for copper the optimum Θ_D value is approximately 335 K. This value was assumed to be the upper limit for a Cu–15 at.% Zn alloy when determining the contributions to the intensity of this alloy. The results of calorimetric measurements of Θ_D for Cu–Zn α-solid solutions [11] demonstrate that Θ_D of the alloy reduces with an increase in the Zn content. Knowing the Θ_D concentration behavior in the alloy, the lower Θ_D limit can also be estimated. Since the intensity grows as Θ_D decreases, then, at a certain Θ_D value in some scattering angle ranges, the difference between the measured intensity and the intensity computed without regard for short-range order parameters and the size effect will be below zero and this is unlikely. Calculations have shown that $\Theta_{D\,\min} = 310$ K. Therefore, for the Cu–15 at.% Zn alloy we have chosen $\Theta_D = 320$ K. At the same time, the value of Θ_D measured calorimetrically is 345.2 K, and for a Cu–17.4 at.% Zn it was found to be 332.7 K. The ratio of the two values is 1.037. Division of Θ_D for copper by 1.037 yields $\Theta_D = 323$ K for the Cu–15 at.% Zn alloy. The value of Θ_D for a Cu–15 at.% Ni alloy was arrived at in the same way. No calorimetric measurements of Θ_D were made for this alloy, but elastic constants C_{11}, C_{22}, and C_{33} for a Cu–9.7 at.% Ni alloy were determined experimentally [11]. It is known [14] that elastic constants may be used to calculate, to a sufficient accuracy, the calorimetric Debye temperatures. From the Launey tables [14] we find $\Theta_D = 345$ K. This value differs from the calorimetric temperature Θ_D for copper by a mere 2%. It can therefore be inferred that, in a Cu–Ni solid solution, the Debye temperature is weakly dependent on the concentration in the range of low Ni concentrations. For this reason, when computing the short-range order parameters in a Cu–15 at.% Ni alloy, its Debye temperature can be assumed approximately equal to the Debye temperature of Cu determined by comparing the theoretical and measured intensities of X-ray diffuse scattering by copper (see Fig. 1).

In a number of studies, X-ray diffuse scattering caused by static displacements was considered auxiliary and eliminated by calculation. In this case, the researchers used a continuum model or the method proposed by Warren [5] where the quadratic size effect was assumed negligible. The microscopic approach in [6] did not include the impact of ordering on the size effect.

The intensity of X-ray diffuse scattering by polycrystalline solid solutions can be written as

$$\begin{aligned} I(x) = NC_AC_B\Bigg\{ \sum_{i=1} \alpha \left[\Delta f^2 J_0\left(\frac{2\pi}{a} x r_i\right) - 2\Delta f \langle f\rangle F_i^{(1)}(x)\beta + \langle f\rangle^2 F_i^{(2)}(x)\beta^2\right] \\ - \Delta f \langle f\rangle F_0^{(1)}(x) + \langle f^2\rangle F_0^{(2)}(x)\beta^2 \Bigg\} = \sum_{i=1} \alpha_i I_i^{\text{theor}}(x), \end{aligned} \tag{1}$$

where C_A and C_B are the concentrations of elements A and B, respectively; α_i is a short-range parameter for the ith coordination sphere; $\Delta f = f_A - f_B$; $<f> = C_A f_A + C_B f_B$; f_A and f_B are the form-factors of X-ray scattering; $x = 2a \sin\theta/\lambda$, θ is the scattering angle, a is the lattice constant; λ is the wavelength; r_i is the radius of the ith coordination sphere; $F_i^{(1)}(x)$ and $F_i^{(2)}(x)$ are respectively the modulating functions of the linear and quadratic size effects for the ith coordination sphere; J_0 is the zero-order Bessel function; $\beta = (1/V)(\partial V/\partial C)$, V is the unit cell volume; and I_i^{theor} is the theoretical intensity values for the ith coordination sphere.

For alloys with close atomic numbers, the basic contribution to X-ray diffuse scattering is made by the third term in formula (1), and this contribution is large when $x \geq 2$. Usually, only $F_0^{(1)}$ and $F_0^{(2)}$ were used in processing of experimental data, and measurements were carried out at small θ for which contribution of the first term in square brackets of formula (1) is substantial if the difference between f_A and f_B is significant. To estimate the short-range order parameters in terms of the intensity of X-ray diffuse scattering reduced to electron units, the contribution of auxiliary scattering (Compton, double Bragg, thermal scattering, and Laue background) was subtracted from the intensity. The values of α_i can be found from the minimum condition for the squared difference,

$$\sum_l \left| \Delta I^{\text{exp}}(x_l) - \sum_i I_i(x_l)\alpha_i \right|^2 = \min. \tag{2}$$

The authors of [15] considered different approximations with account of static lattice distortions to describe contributions of the size effect and the correlations in the arrangement of atoms to the intensity of X-ray diffuse scattering of polycrystalline fcc and bcc alloys. It was shown, in particular, that a microscopic approach based on the Born-Begbie model is applicable for this purpose [16, 17]. However, in this case, it is first required to calculate modulating functions of the linear and quadratic size effects. The elastic constants that we used for our alloys were taken from [2]. The tables of the size effect modulating functions for a set of ratios C_{12}/C_{11} and C_{44}/C_{11} are presented in [15].

RESULTS

Figure 2 depicts the intensities of X-ray diffuse scattering measured in the Cu–15 at.% Zn and Cu–15 at.% Ni alloys as functions of the dimensionless quantity x. The difference of intensities for the same angles varies significantly with the growth of the angle θ which cannot be explained only by a difference in the scattering power of atoms and different Debye temperatures of the components. On the contrary, since the atomic factor of Ni is smaller and its Debye temperature is higher than those of Cu and Zn, and the difference between the diameters of a Ni atom and a Cu atom is smaller than that between the diameters of Zn and Cu atoms, the scattering intensity in the Cu–15 at.% Zn alloy should have been higher as compared with the Cu–15 at.% Ni alloy throughout the range of angles θ. Yet, as follows from Fig. 2, this is not the case. If intensities are close in the interval of angles between structural peaks (200)–(220) and (222)–(311), except for a region in the vicinity of the structural peaks, the intensity in the Cu–15 at.% Ni alloy in the (222)–(400) range is higher than that in the Cu–15 at.% Zn alloy, whereas in the (400)–(311) range this intensity is lower. This can solely be attributed to the correlation in the arrangement of component atoms that has been shown to exert a strong effect on diffuse scattering, especially, due to the size effect at large scattering angles.

The results of measuring the X-ray diffuse scattering intensity for the Cu–15 at.% Zn alloy as a function of x are shown in Fig. 3. Figure 3 also presents the intensity synthesized curve computed with account of the size effect and the short-range order parameters obtained by minimizing the squared difference in formula

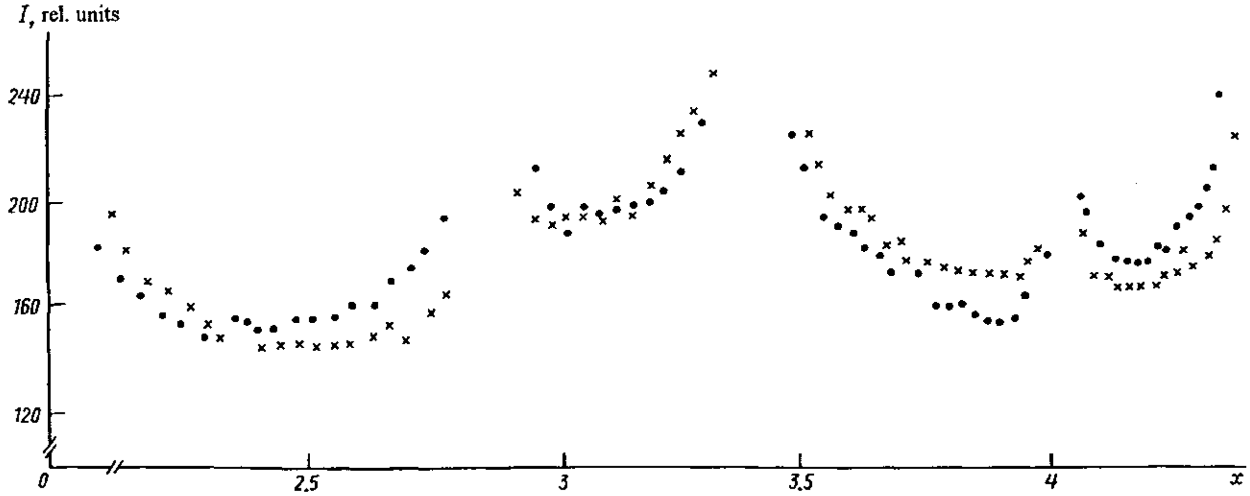

Fig. 2

Intensity of X-ray diffuse scattering vs. $x = 2a\sin\theta/\lambda$ in Cu–15 at.% Zn (dots) and Cu–15 at.% Ni (crosses) alloys.

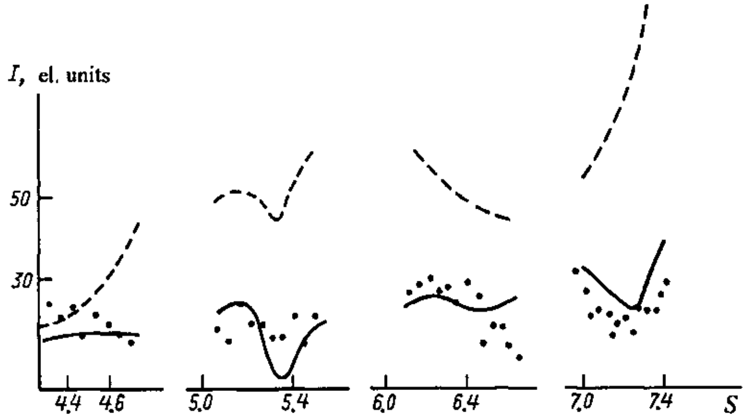

Fig. 3

Intensity of X-ray diffuse scattering in Cu–15 at.% Zn alloy vs. $S = 4\pi\sin\theta/\lambda$: experiment (dots), synthesized curves with account of size effect and short-range order (solid) and size effect only (dashed).

(2) and the synthesized curve that takes into account only the size effect, without correlation. The X-ray diffuse scattering intensity for the Cu–15 at.% Zn alloy was measured at a distance from the structural peaks (200), (311), (222), (400) and (331) to minimize their influence. Comparing the curves brings out clearly that neglecting the correlations contribution to the arrangement of atoms overestimates considerably the synthesized intensities. Alternatively, when ordering is taken into account, the synthesized curve obtained by means of calculated short-range order parameters (see Table 1) approaches the experimental values of diffuse scattering intensity.

It follows from Fig. 3 that there is no exact coincidence in the second and fourth ranges. This can be attributed to a measurement error and the difficulties of taking into consideration both point and extended defects always present in an alloy. The computed values of short-range order parameters indicate a substantial short-range order, and the sign of α_1 shows that a short-range order of the TiAl type is realized in a Cu–15 at.% Zn α-solid solution at room temperature. The data obtained are in agreement with the

Table 1

Experimental Short-Range Order Parameters α_i of Cu–15 at.% Zn and Cu–15 at.% Ni Alloys

Alloy	α_1	α_2	α_3	α_4	α_5	α_0
Cu–15 at.% Zn	–0.17	0.32	0.12	– 0.43	– 0.06	0.38
Cu–15 at.% Ni	0.14	0.50	– 0.65	0.60	– 0.06	0.46
Cu–15 at.% Ni (additional annealing at 700 °C for 10 h)	0.05	– 0.08	– 0.28	0.52	– 0.09	0.10
Cu–20 at.% Ni [2]	0.12	– 0.01	0.01	0.01	—	—

experimental results on electrical resistance, thermal e. m. f., and other physical properties [18] that also essentially depend on atomic correlation.

To study the effect of the ordering type on the scattering intensity in alloys with close atomic numbers, measurements were carried out on a Cu–15 at.% Ni alloy sample previously strained and annealed at 700 °C for 10 h with subsequent water hardening. Figure 4 presents the experimental values less auxiliary scattering and the synthesized curve (taking into account the calculated short-range order parameters α_i, see Table 1). Comparing the curves shown in Figs. 3 and 4 demonstrates that correlation in the arrangement of atoms affects differently the diffuse scattering intensity in the Cu–15 at.% Zn and Cu–15 at.% Ni alloys. The computed values of the short-range order parameters for the Cu–15 at.% Ni alloy agree well with the neutron diffraction data (see Table 1). However, the values we have obtained for the second and subsequent coordination spheres are higher than the neutron diffraction data [2]. This can be attributed to the specimen strain in polishing. Measurements made after annealing at 700 °C for 10 h demonstrated, as a consequence, a lower diffusion background and lower values of the parameters. The sign of parameter α_1 found by the X-ray diffuse scattering technique for the Cu–15 at.% Ni alloy is indicative of short-range stratification in this alloy.

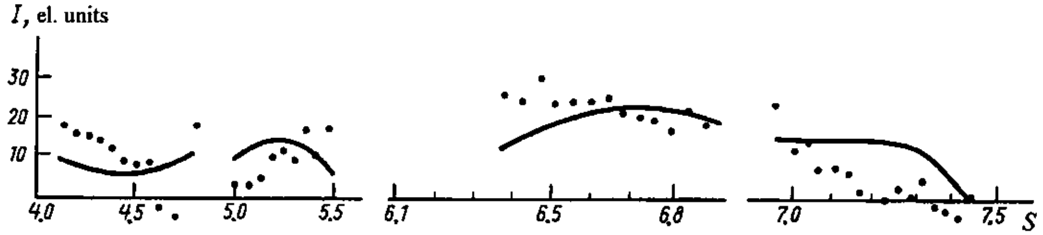

Fig. 4

Intensity of X-ray diffuse scattering in Cu–15 at.% Ni alloy vs. $S = 4\pi \sin\theta/\lambda$: experiment (dots), and synthesized curve accounting for size effect and short-range order (dashed line).

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Department of Solid-State Physics